Chapter 6
Thermodynamics

NCERT Exercise

Question 1:

Choose the correct answer. A thermodynamic state function is a quantity
(i) used to determine heat changes
(ii) whose value is independent of path
(iii) used to determine pressure volume work
(iv) Whose value depends on temperature only.

Solution 1:

A thermodynamic state function is a quantity whose value is independent of a path. Functions like p, *V*, *T* etc. depend only on the state of a system and not on the path. Hence, alternative (ii) is correct.

Question 2:

For the process to occur under adiabatic conditions, the correct condition is:
(i) $\Delta T = 0$
(ii) $\Delta p = 0$
(iii) $q = 0$
(iv) $w = 0$

Solution 2:

A system is said to be under adiabatic conditions if there is no exchange of heat between the system and its surroundings. Hence, under adiabatic conditions, $q = 0$. Therefore, alternative (iii) is correct.

Question 3:

The enthalpies of all elements in their standard states are:
(i) unity
(ii) zero
(iii) < 0
(iv) different for each element

Solution 3:

The enthalpy of all elements in their standard state is zero. Therefore, alternative (ii) is correct.

Question 4:

ΔU^{θ} of combustion of methane is - X kJ mol^{-1}. The value of ΔH^{θ} is

(i) = ΔU^{θ}

(ii) > ΔU^{θ}

(iii) < ΔU^{θ}

(iv) = 0

Solution 4:

Since $\Delta H^{\theta} = \Delta U^{\theta} + \Delta n_g RT$ and $\Delta U^{\theta} = -X$ kJ mol^{-1},

$\Delta H^{\theta} = (-X) + \Delta n_g RT.$

$\Rightarrow \Delta H^{\theta} < \Delta U^{\theta}$

Therefore, alternative (iii) is correct.

Question 5:

The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are, -890.3 kJ mol^{-1} ,-393.5 kJ mol^{-1}, and -285.8 kJ mol^{-1} respectively. Enthalpy of formation of $CH_4(g)$ will be

(i) -74.8 kJ mol^{-1} (ii) -52.27 kJ mol^{-1}

(iii) +74.8 kJ mol^{-1} (iv) +52.26 kJ mol^{-1}.

Solution 5:

According to the question,

(i)

$$CH_4(g)+2O_2(g)\rightarrow CO_2(g)+2H_2O(l);\ \Delta_c H^{\ominus} = -890.3 kJ\ mol^{-1}$$

(ii)

$$C(s)+O_2(g)\rightarrow CO_2(g);\ \Delta_c H^{\ominus} = -393.5 kJ\ mol^{-1}$$

(ii)

$$2H_2(g)+O_2(g)\rightarrow 2H_2O(l);\ \Delta_c H^{\ominus} = -285.8 kJ\ mol^{-1}$$

Thus, the desired equation is the one that represents the formation of $CH_4(g)$ i.e.,

$$C(s)+2H_2(g)\rightarrow CH_4(g);\ \Delta_f H_{Ch_4} = \Delta_C H_C + 2\Delta_C H_{h_2} - \Delta_C H_{Co_2}$$

$$= (-393.5) + 2*(-285.8) - (-890.3) = -74.8 kJmol^{-1}$$

$\therefore$ Enthalpy of formation of $CH_4(g)$ = -74.8 kJ mol-1

Hence, alternative (i) is correct

Question 6:

A reaction, A + B $\rightarrow$C + D + q is found to have a positive entropy change. The reaction will be

(i) possible at high temperature
(ii) possible only at low temperature
(iii) not possible at any temperature
(iv) possible at any temperature

Solution 6:

For a reaction to be spontaneous, ΔG should be negative.
$\Delta G = \Delta H - T\Delta S$
According to the question, for the given reaction,
ΔS = positive
ΔH = negative (since heat is evolved) $\Rightarrow$ ΔG = negative
Therefore, the reaction is spontaneous at any temperature.
Hence, alternative (iv) is correct.

Question 7:

In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process?

Solution 7:

According to the first law of thermodynamics,
$\Delta U = q + W$ (i)
Where,
ΔU = change in internal energy for a process
q = heat
W = work
Given,
q = + 701 J (Since heat is absorbed)
W = -394 J (Since work is done by the system
Substituting the values in expression (i), we get
$\Delta U = 701 \text{ J} + (-394 \text{ J})$
$\Delta U = 307 \text{ J}$
Hence, the change in internal energy for the given process is 307 J.

Question 8:

The reaction of cyanamide, $NH_2CN(s)$ with dioxygen was carried out in a bomb calorimeter and ΔU was found to be -742.7 KJ mol^{-1} at 298 K. Calculate the enthalpy change for the reaction at 298 K.

$$NH_2CN_{(g)} + \frac{3}{2}O_2(g) \rightarrow N_{2(g)} + CO_{2(g)} + H_2O_{(l)}$$

Solution 8:

Enthalpy change for a reaction (ΔH) is given by the expression,

$$\Delta H = \Delta U + \Delta_{ng} RT$$

Where,
ΔU = change in internal energy
Δn_g = change in number of moles
For the given reaction,
$\Delta n_g = \Sigma n_g$ (products) - Σn_g (reactants)
= (2 - 1.5) moles
Σn_g = +0.5 moles
And, $\Delta U = -742.7$ kJ mol^{-1}
T = 298 K
R = 8.314×10^{-3} kJ mol^{-1} K^{-1}
Substituting the values in the expression of ΔH:
$\Delta H = (-742.7 \text{ kJ mol}^{-1}) + (+0.5 \text{ mol}) (298 \text{ K})\ 8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$
= -742.7 + 1.2
$\Delta H = -741.5 \text{kJ mol}^{-1}$

Question 9:

Calculate the number of kJ of heat necessary to raise the temperature of 60 g of aluminium from 35°C to 55°C. Molar heat capacity of Al is 24 J mol^{-1} K^{-1}.

Solution9:

From the expression of heat (q),
q = m. c. ΔT
Where,
c = molar heat capacity
m = mass of substance
ΔT = change in temperature
Substituting the values in the expression of

$$q=\left(\frac{60}{27}mol\right)\left(24\,J\,mol^{-1}K^{-1}\right)\left(20K\right)$$

q = 1066.7J

q= 1.07 kJ

Question 10:

Calculate the enthalpy change on freezing of 1.0 mol of water at 10.0°C to ice at - 10.0°C. ,Δ_{fus} H = 6.03 KJ mot^{-1} at 0°C.

C_p [$H_2O(l)$] = 75.3 J mol^{-1} K^{-1};

C_p [$H_2O(s)$] = 36.8 J mol^{-1} K^{-1}.

Solution 10:

Total enthalpy change involved in the transformation is the sum of the following changes:

(a) Energy change involved in the transformation of 1 mol of water at 10°C to 1 molof water at 0°C.

(b) Energy change involved in the transformation of 1 mol of water at 0° to 1 mol of ice at 0°C.

(c) Energy change involved in the transformation of 1 mol of ice at 0°C to 1 mol of ice at 10°C.

$$Total\,\Delta H = C_p\left[H_2O(l)\right]\Delta T + \Delta H_{freezing} + C_p\left[H_2O(s)\right]\Delta T$$

= (75.3 J mol^{-1} K^{-1}) (0 - 10)K + (-6.03 × 10^3 J mol^{-1}) + (36.8 J mol^{-1} K^{-1}) (-10 - 0)K

= -753 J mol^{-1} - 6030 J mol^{-1} - 368 J mol^{-1}

= -7151 J mol^{-1}

= -7.151 kJ mol^{-1}

Hence, the enthalpy change involved in the transformation is -7.151 kJ mol^{-1}

Question 11:

Enthalpy of combustion of carbon to carbon dioxide is -393.5 kJ mol^{-1} Calculate the heat released upon formation of 35.2 g of CO_2 from carbon and dioxygen gas.

Solution 11:

Formation of CO_2 from carbon and dioxygen gas can be represented as

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)};\Delta H = -393.5\,kJ\,mol^{-1}$$

(1mole=44g)

Heat released in the formation of 44 g of CO_2 = 393.5 KJmol^{-1}

Heat released in the formation of 35.2 g of
$CO_2 = (393.5\,KJ) \times (35.2\,g)/(44\,g) = 314.8\,KJ$

Question 12:

Enthalpies of formation of CO(*g*), CO$_2$(*g*), N$_2$O(*g*)and N$_2$O$_4$(*g*) are -110 ,-393, 81 kJ and 9.7 kJ mol^{-1} respectively. Find the value of $\Delta_r H$ for the reaction:

$$N_2O_{4(g)} + 3CO(g) \longrightarrow N_2O(g) + 3CO_{2(g)}$$

Solution 12:

$\Delta_r H$ for a reaction is defined as the difference between $\Delta_f H$ value of products and $\Delta_f H$ value of reactants.

$$\Delta_r H = \sum \Delta_f H(product) - \sum \Delta_f H(reac\tan t)$$

For the given reaction,

$$N_2O_{4(g)} + 3CO(g) \longrightarrow N_2O(g) + 3CO_{2(g)}$$

$$\Delta_r H = \left[\{\Delta_f H(N_2O) + 3\Delta_f H(CO_2)\} - \{\Delta_f H(N_2O) + 3\Delta_f H(CO)\}\right]$$

Substituting the values of $\Delta f H$ for N$_2$O, CO$_2$, N$_2$O$_4$, and CO from the question, we get:

$$\Delta_r H = \left[\{81 kJ\ mol^{-1} + 3(-393) KJ\ mol^{-1}\} - \{9.7 kJ\ mol^{-1} + 3(-110) KJ\ mol^{-1}\}\right]$$

$$\Delta_r H = -777.7 kJmol^{-1}$$

Hence, the value of $\Delta r H$ for the reaction is $-777.7 kJmol^{-1}$.

Question 13:

Given

$$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)};\ \Delta_r H^\theta = \text{-}92.4\ kJ\ \ mol^{-1}$$

What is the standard enthalpy of formation of NH$_3$ gas?

Solution 13:

Standard enthalpy of formation of a compound is the change in enthalpy that takes place during the formation of 1 mole of a substance in its standard form from its constituent elements in their standard state.

Re-writing the given equation for 1 mole of NH$_3$(*g*),

$$\frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2(g)} \longrightarrow 2NH_{3(g)}$$

∴ Standard enthalpy of formation of $NH_3(g)$

$= \frac{1}{2} \Delta_r H^\theta$

$= \frac{1}{2} (-92.4 \text{ kJ mol}^{-1})$

$= -46.2 \text{ kJ mol}^{-1}$

Question 14:

Calculate the standard enthalpy of formation of $CH_3OH(l)$ from the following data:

$$CH_3OH_{(l)} + \frac{3}{2}O_2(g) \longrightarrow CO_{2(g)} + 2H_2O_{(l)} \ ; \ \Delta_r H^\theta = -726 \ kJ \ mol^{-1}$$

$$C_{(g)} + O_{2(g)} \longrightarrow CO_{2(g)} \ ; \ \Delta_c H^\theta = -393 \ kJ \ mol^{-1}$$

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)} \ ; \ \Delta_f H^\theta = -286 \ kJ \ mol^{-1}.$$

Solution 14:

The reaction that takes place during the formation of $CH_3OH(l)$ can be written as:

$$C(s) + 2H_2O(g) + \frac{1}{2}O_2(g) \longrightarrow CH_3OH(l) \ (\mathbf{1})$$

The reaction (**1**) can be obtained from the given reactions by following the algebraic calculations as:

Equation (ii) + 2 × equation (iii) - equation (i)

$\Delta_f H^\theta [CH_3OH(l)] = \Delta c H^\theta + 2\Delta_f H^\theta [H2O(l)] - \Delta r H^\theta$

$= (-393 \text{ kJ mol}^{-1}) + 2(-286 \text{ kJ mol}^{-1}) - (-726 \text{ kJ mol}^{-1})$

$= (-393 - 572 + 726) \text{ kJ mol}^{-1}$

∴ $\Delta_f H^\theta [CH_3OH(l)] = -239 \text{ kJ mol}^{-1}$

Question 15:

Calculate the enthalpy change for the process

$CCl_4(g) \rightarrow C(g) + 4Cl(g)$

and calculate bond enthalpy of C-Cl in $CCl_4(g)$.

$\Delta_{vap} H^\theta (CCl_4) = 30.5 \text{ kJ mol}^{-1}$.

$\Delta_f H^\theta (CCl_4) = -135.5 \text{ kJ mol}^{-1}$.

$\Delta_a H^\theta (C) = 715.0 \text{ kJ mol}^{-1}$, where $\Delta a H^\theta$ is enthalpy of atomisation

$\Delta_a H^{\theta}$ (Cl_2) = 242 kJ mol^{-1}

Solution 15:

The chemical equations implying to the given values of enthalpies are:

$$(i)\ \ CCl_{4(l)} \longrightarrow CCl_{4(g)} \Delta_{vap} H^{\theta} = 30.5 kJ\ \ mol^{-1}$$

$$(ii)\ \ C_{(s)} \longrightarrow C_{(g)} \Delta_a H^{\theta} = 715.0\ kJ\ \ mol^{-1}$$

$$(iii)\ \ Cl_{2(g)} \longrightarrow 2Cl_{(g)} \Delta_a H^{\theta} = 242\ kJ\ \ mol^{-1}$$

$$(iv)\ \ C_{(g)} + 4Cl_{(g)} \longrightarrow CCl_{4(g)} \Delta_f H = -135.5\ kJ\ \ mol^{-1}$$

Enthalpy change for the given process $CCl_{4(g)} \longrightarrow C_{(g)} + 4Cl_{(g)}$ can be calculated using the following algebraic calculations as:

Equation (ii) + 2 × Equation (iii) - Equation (i) - Equation (iv)

$\Delta H = \Delta_a H^{\theta}(C) + 2\Delta_a H^{\theta}(Cl2) - \Delta_{vap} H^{\theta} - \Delta_f H$

= (715.0 kJ mol^{-1}) + 2(242 kJ mol^{-1}) - (30.5 kJ mol^{-1}) - (-135.5 kJ mol^{-1})

$\therefore \Delta H$ = 1304 kJ mol^{-1}

Bond enthalpy of C-Cl bond in CCl_4 (*g*)

$$= \frac{1304}{4} kJ\ mol^{-1}$$

= 326 kJ mol^{-1}

Question 16:

For an isolated system, $\Delta U = 0$, what will be ΔS?

Solution 16:

ΔS will be positive i.e., greater than zero.

Since $\Delta U = 0$, ΔS will be positive and the reaction will be spontaneous.

Question 17:

For the reaction at 298 K,

2A + B → C

ΔH = 400 kJ mol^{-1} and ΔS = 0.2 kJ K^{-1} mol^{-1}

At what temperature will the reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range?

Solution 17:

From the expression,
$\Delta G = \Delta H - T\Delta S$
Assuming the reaction at equilibrium, ΔT for the reaction would be:

$$T = (\Delta H - \Delta G)\frac{1}{\Delta S}$$

$$= \frac{\Delta H}{\Delta S}$$

($\Delta G = 0$ at equilibrium)

$$= \frac{400 kJ\ mol^{-1}}{0.2 kJ\ K^{-1} mol^{-1}}$$

$T = 2000$ K
For the reaction to be spontaneous, ΔG must be negative. Hence, for the given reaction to be spontaneous, T should be greater than 2000 K.

Question 18:
For the reaction,

$$2Cl(g) \rightarrow Cl_2(g)$$

what are the signs of ΔH and ΔS ?

Solution 18:
ΔH and ΔS are negative
The given reaction represents the formation of chlorine molecule from chlorine atoms. Here, bond formation is taking place. Therefore, energy is being released. Hence, ΔH is negative.
Also, two moles of atoms have more randomness than one mole of a molecule. Since spontaneity is decreased, ΔS is negative for the given reaction.

Question 19: For the reaction $2A(g) + B(g) \rightarrow 2D(g)$

$$2A(g) + B(g) \rightarrow 2D(g)$$

$\Delta U^{\theta} = -10.5$ kJ and $\Delta S^{\theta} = -44.1\ JK^{-1}$.
Calculate ΔG^{θ} for the reaction, and predict whether there action may occur spontaneously.

Solution 19:
For the given reaction,

$$2A(g) + B(g) \rightarrow 2D(g)$$

$\Delta n_g = 2 - (3)$
$= -1$ mole

Substituting the value of ΔU^θ in the expression of ΔH:

$\Delta H^\theta = \Delta U^\theta + \Delta n_g RT$

$= (-10.5 \text{ kJ}) - (-1)(8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1})(298 \text{ K})$
$= -10.5 \text{ kJ} - 2.48 \text{ kJ}$

$\Delta H^\theta = -12.98 \text{ kJ}$

Substituting the values of ΔH^θ and ΔS^θ in the expression of ΔG^θ:

$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$

$= -12.98 \text{ kJ} - (298 \text{ K})(-44.1 \text{ J K}^{-1})$
$= -12.98 \text{ kJ} + 13.14 \text{ kJ}$

$\Delta G^\theta = +0.16 \text{ kJ}$

Since ΔG^θ for the reaction is positive, the reaction will not occur spontaneously.

Question 20:

The equilibrium constant for a reaction is 10. What will be the value of ΔG^θ? R = $8.314 \text{ JK}^{-1} \text{ mol}^{-1}$, $T = 300$ K.

Solution 20:

From the expression,

$\Delta G^\theta = -2.303 RT \log Keq$

ΔG^θ for the reaction,

$= (2.303)(8.314 \text{ JK}^{-1} \text{ mol}^{-1})(300 \text{ K}) \log 10$

$= -5744.14 \text{ Jmol}^{-1}$

$= -5.744 \text{ kJ mol}^{-1}$

Question 21:

Comment on the thermodynamic stability of NO(g), given

$$\frac{1}{2}NO(g) + \frac{1}{2}O_2(g) \rightarrow NO_2(g) : \Delta_r H^\theta = 90 \ kJ \ mol^{-1}$$

$$NO_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow O_{2(g)} : \Delta_r H^{\theta} = -74 kJ\ mol^{-1}$$

Solution 21:

The positive value of $\Delta_r H$ indicates that heat is absorbed during the formation of NO(g). This means that NO(g) has higher energy than the reactants (N_2 and O_2). Hence, NO(g) is unstable.

The negative value of ΔrH indicates that heat is evolved during the formation of NO_2(g) from NO(g) and O_2(g). The product, NO_2(g) is stabilized with minimum energy.

Hence, unstable NO(g) changes to unstable NO_2(g).

Question 22:

Calculate the entropy change in surroundings when 1.00 mol of H_2O(l) is formed under standard conditions. $\Delta_f H^{\theta} = -286$ kJ mol^{-1}.

Solution 22:

It is given that 286 kJ mol^{-1} of heat is evolved on the formation of 1 mol of H_2O(l). Thus, an equal amount of heat will be absorbed by the surroundings.

$q_{surr} = +286$ kJ mol^{-1}

Entropy change ($\Delta Ssurr$) for the surroundings $= \dfrac{q_{Surr}}{7}$

$$= \frac{286 kJ\ mol^{-1}}{298k}$$

$\therefore \Delta Ssurr = 959.73$ J mol^{-1} K^{-1}